49. *Tribromogold.*

By Abraham Burawoy and Charles S. Gibson.

There is no evidence for the existence of the tervalent gold ion (Au^{+++}),* and tervalent gold can exist as part of a tervalent kation only when suitably co-ordinated in such a compound as diethylenediaminogold tribromide, $[Au\ en_2]Br_3$ (Gibson and Colles, J., 1931, 2410).

The organic compounds of gold containing tervalent gold all contain 4-covalent gold and it seemed desirable to determine whether there is any evidence for assigning a constitution to tribromogold analogous to that of organic compounds of tervalent gold which are non-electrolytes. Obviously, such evidence may be obtained from molecular-weight

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* For this reason and as a consequence of the present investigation as well as of the work of other authors, the gold trihalides are more systematically named, for example, as trichlorogold and tribromogold.

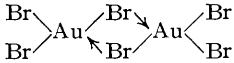
determinations of tribromogold prepared as described by Gibson and Colles (*loc. cit.*). Fischer has found the molecular formula of "auric chloride" vapour between 150° and 260° to be Au_2Cl_6 (*Z. anorg. Chem.*, 1929, **184**, 333).

Although tribromogold is stable in bromoform and in bromine, its solubility in these liquids at their melting points is far too small to permit of molecular-weight determinations by the cryoscopic method. Even at the boiling point, the solubility of tribromogold in bromine (in which its dissociation must be negligible) is still small, but this seems to be the only solvent in which direct determinations of the molecular weight are possible.

The method employed was that of Beckmann (*Z. physikal. Chem.*, 1902, **40**, 129; 1903, **44**, 164), in which the solution is heated by the vapour of the solvent boiling in an outer jacket, allowing, for a given weight of solute, four determinations of the molecular weight to be made with 7·4, 10·8, 14·2, and 17·5 c.c. of solution at the boiling point. The apparatus was constructed entirely of glass and a Beckmann micro-thermometer made to suit the apparatus was used, the bulb being always completely immersed in the solution. The molecular elevation of the boiling point of bromine was assumed to be 52 (Beckmann, *Z. physikal. Chem.*, 1900, **46**, 853), and the density of bromine at the boiling point 2·948. The following are two typical series of results :

(1) With 0·2100 g. : Δ 0·048°, 0·033°, 0·035°, 0·020°; *M*, 1043, 1039, 1058, 745.
(2) With 0·2569 g. : Δ 0·062°, 0·047°, 0·045°, 0·032°; *M*, 987, 892, 809, 709.

The average value for the molecular weight of tribromogold thus found is approximately 910 [Calc. for $(AuBr_3)_2$: *M*, 874].

The experimental error in any one determination is large. In the two series of results recorded, the highest elevation of the boiling point observed was 0·062° and the lowest 0·020° and there may be an error as high as 0·005° in the actual observation. In spite of this, the experiments show that the molecular weight of tribromogold is twice that demanded by its empirical formula. This implies that the constitution of the compound may be expressed by the formula . Tribromogold thus has a constitution analogous to that of the organic compounds of tervalent gold in which the gold atoms are 4-covalent and which are non-electrolytes.*

No evidence of the formation of an ethoxy-derivative of gold (or of a pyridine derivative of such a compound) has been obtained by allowing a strongly cooled suspension of tribromogold in ether to react with either 2 or 3 mols. of potassium ethoxide in alcoholic solution. In the former case, potassium bromide and a small quantity of gold having been removed, the brownish red filtrate was treated with pyridine and the greyish precipitate produced was recrystallised from pyridine below 40° or, better, by addition of ether to the pyridine solution; the product separated in colourless crystals of *monopyridinomonobromogold*, Py→Au–Br, decomposing above 120° or on standing or on heating with solvents, including pyridine (Found : Au, 54·7. C_5H_5NBrAu requires Au, 55·3%). In the latter case, the tribromogold was quantitatively reduced to gold, and potassium bromide (3 mols.) obtained.

When pyridinotribromogold (Gibson and Colles, *loc. cit.*) reacted under similar conditions with potassium ethoxide (2 mols.), the red gold compound was converted into a yellowish-grey mixture of potassium bromide and monopyridinomonobromogold. The latter was extracted with pyridine, the pyridine solution evaporated at the ordinary temperature over sulphuric acid, and the residue purified by precipitation from pyridine solution with ether. It was monopyridinomonobromogold, identical with that previously obtained (Found : Au, 54·7%).

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* The magnetic susceptibility of tribromogold, kindly determined by Professor S. Sugden, F.R.S. (J., 1932, 161), is $\chi = -0{\cdot}23 \times 10^{-6}$ e.m.u. at 19°, confirming the diamagnetic nature of the compound.